

# Two modes of change in Southern Ocean productivity over the past million years

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**Export of organic carbon from surface waters of the Antarctic zone of the Southern Ocean decreased during the last ice age, coinciding with declining atmospheric CO<sub>2</sub> concentrations, signaling reduced exchange of CO<sub>2</sub> between the ocean interior and the atmosphere. In contrast, in the Subantarctic Zone, export production increased into ice ages coinciding with rising dust fluxes and thus suggesting iron fertilization of Subantarctic phytoplankton. Here, a new high-resolution productivity record from the Antarctic zone is compiled with parallel Subantarctic data over the last million years. Together, they fit the view that the combination of these two modes of Southern Ocean change determines the temporal structure of the glacial/interglacial atmospheric CO<sub>2</sub> record, including during the interval of “lukewarm” interglacials between 450 and 800 thousand years ago.**

Antarctic ice core measurements reveal that regional air temperatures and atmospheric  $p\text{CO}_2$  were tightly correlated over glacial-interglacial cycles of the past 800 kyrs (1). Many studies have inferred a dominant role for the Southern Ocean in modulating glacial-interglacial variability of atmospheric  $p\text{CO}_2$  ((2) and references therein). The central role of the Southern Ocean is thought to reflect its leverage on the global efficiency of the biological pump, in which the production, sinking, and deep

31 remineralization of organic matter sequesters carbon in the ocean interior, lowering  
32 atmospheric CO<sub>2</sub>. Dense subsurface water masses outcrop in the Southern Ocean,  
33 providing exchange pathways between the deep ocean and the atmosphere. Vertical  
34 exchange of water causes deeply sequestered CO<sub>2</sub> and nutrients to be mixed to the  
35 surface, fueling high rates of phytoplankton productivity. Today, the Southern Ocean is  
36 the principal leak in the biological pump, because export production is inadequate to  
37 prevent the evasion of deeply sequestered carbon when waters are exposed to the  
38 atmosphere. The polar CO<sub>2</sub> leak can be directly inhibited during glacial stages by factors  
39 such as increased sea-ice cover (3) and/or changes in buoyancy forcing and convection  
40 (4, 5). In addition, the glacial CO<sub>2</sub> reduction associated with these mechanisms would  
41 have been amplified by iron fertilization of the Subantarctic Zone (SAZ) of the Southern  
42 Ocean (6, 7) and associated alkalinity feedbacks (8).

43 Export production records from the Antarctic Zone (AZ) have been used to trace  
44 changes in the rate of Southern Ocean overturning through time (9, 10). However, these  
45 records only cover the last glacial cycle, restricting our understanding of the evolution of  
46 the Antarctic component of this two-mode system by which the Southern Ocean regulates  
47 the transfer of carbon between the ocean interior and the atmosphere over previous  
48 climatic cycles. Here, we report a high-resolution relative elemental concentration record  
49 from Ocean Drilling Program (ODP) site 1094 (53.2°S, 05.1°E; water depth 2,850 m)  
50 (Fig. 1), which traces changes in AZ export production over the past million years (SOM,  
51 Figs S1 & S2). The time resolution achieved here rivals the measurement density typical  
52 for Antarctic ice-core records. These observations are complemented with reconstruction  
53 of <sup>230</sup>Th-normalized biogenic particle flux to the seafloor covering the last two glacial  
54 terminations (Fig. 2).

55 The pelagic sediment analyzed in this study is dominantly composed of  
56 diatomaceous opal and terrigenous detritus, the latter of which is mostly ice-rafted, with a  
57 minor contribution from aeolian material (11). Assuming that sedimentary iron (Fe) is of  
58 detrital origin, barium (Ba) abundance normalized to Fe yields an estimate of the  
59 sedimentary concentration of biogenic (or excess) Ba (bioBa), which serves as a tool to  
60 reconstruct changes in the integrated flux of organic matter to the sediment (12).  
61 Normalization by Fe assumes that the detrital fraction has not varied significantly in

space and time, supported by provenance studies, indicating that the tephra-rich terrigenous material at this site is consistently derived from the South Sandwich volcanic arc, with negligible contribution from Bouvet Island and possibly the Antarctic Peninsula (11). Calcium (Ca) normalized to Fe indicates the sedimentary concentration of biogenic carbonate ( $\text{CaCO}_3$ ). The records of Fe and Ti show almost identical trends in amplitude, but XRF signals are better for Fe, which is thus used for normalization. In these opal-rich sediments, elemental spectrum processing does not allow proper quantification of Al because of the overlapping Si peaks, precluding the use of Al as a normalizing agent.

The Ba/Fe record shows a strong climate-related signal (Fig. 3C), with high values during interglacials and lower values during cold stages. The Ba/Fe record is in good agreement with the  $^{230}\text{Th}$ -normalized flux of bioBa (Fig. 2C), supporting the use of Ba/Fe to infer bioBa throughout the record. The large-scale Ba variations cannot be explained as the result of bacterially-mediated sulfate reduction and associated diagenetic barite ( $\text{BaSO}_4$ ) dissolution because no significant sulfate reduction is observed in the interstitial water of Pleistocene sediments of ODP site 1094 (13). Indeed, the  $^{230}\text{Th}$ -normalized flux of bioBa is similar to that of opal and chlorophyll transformation products (chlorins) measured in the same sediment core (Fig. 2). Preservation of these independent paleo-productivity proxies is favored in different sedimentary environments. While the preservation of bioBa can be compromised by reducing conditions, the preservation of organic matter in general, and chlorins in particular, is enhanced when oxygen content is low (14). The preservation of opal is unrelated to the redox state of sediments but primarily driven by the total sedimentation rate (15). The correlation between opal fluxes and excess  $^{231}\text{Pa}/^{230}\text{Th}$  at the same core site during the last 25 kyrs (9) and the correlation between opal fluxes and bioBa over the last 150 kyrs reported here indicate that the reconstructed opal fluxes most likely represent variable production by diatoms.

Consequently, the sedimentary Ba/Fe is interpreted to indicate lower bioBa accumulation and thus less export of organic matter from the surface ocean during cold periods, with the lowest bioBa concentrations coinciding almost exclusively with the glacial maxima, consistent with measurements elsewhere in the Southern Ocean, south of the polar frontal zone ((16) and references therein) (Fig. S3). Sea-ice has the potential to

93 directly alter export production, by blocking sunlight vital for phytoplankton to undertake  
94 photosynthesis; however, sea-ice was only present at this site during the winters of glacial  
95 periods (17), not during the summer growing season. Rather, changes in export imply a  
96 reduced supply of nutrients to the surface ocean. Phytoplankton growth is inhibited by the  
97 lack of bioavailable Fe in most parts of the Southern Ocean. Vertical mixing and  
98 upwelling (rather than atmospheric fluxes) appear to dominate the supply of Fe to the  
99 Antarctic surface ocean at present (18). Thus, glacial decrease in productivity may have  
100 been driven by a reduction in this deep water-derived iron supply.

101 While various physical mechanisms have been proposed for a reduction in this  
102 deep water exposure, they all involve reduction of wind-driven upwelling, wintertime  
103 vertical mixing, or both (4, 5, 19). Upwelling could be lowered by weaker westerlies  
104 and/or by a more northerly position for them, while wintertime vertical mixing is  
105 sensitive to upper ocean density stratification. Various processes can affect this  
106 stratification, including upwelling, which strips away the freshwater cap (halocline) that  
107 maintains vertical stability.

108 Of the nitrate imported into the Antarctic surface today, only a portion derives  
109 from Ekman upwelling, with the remaining deriving from wintertime vertical mixing  
110 (20). Given that the data suggest many fold lower export production during peak ice ages,  
111 we infer that these changes in productivity likely require both a reduction in wind-driven  
112 upwelling and an increase in density stratification. This is significant in that the latter  
113 change would affect deep water formation, through which the Antarctic has its greatest  
114 direct leverage on atmospheric CO<sub>2</sub> (21, 22).

115 Upon glacial terminations, large pulses of export production coincide with  
116 prominent increases in atmospheric CO<sub>2</sub> concentrations reconstructed from Antarctic ice  
117 cores (Figs. 2 & 3). Flux determinations of three independent export production proxies  
118 suggest that the export of organic matter increased by more than an order of magnitude  
119 across the two last climate transitions (Fig. 2). Reconstruction of past silicon and nitrogen  
120 dynamics suggest that relative nutrient utilization did not rise sharply at the last glacial  
121 termination (23), such that the rise in Ba and opal flux was a response to a large increase  
122 in the nutrient supply to the euphotic zone. These increases in export were accompanied  
123 by summer sea-surface temperature (SST) overshoots and abrupt disappearances of

winter sea-ice (17). Summer SSTs increased by more than 4°C in less than 5 kyrs for the last five glacial terminations (17). While the sequence of deglacial events remains to be resolved (9), the systematic and repeated glacial-to-interglacial rises in biogenic flux (Fig. 3) point to a robust pattern of enhanced Southern Ocean overturning during interglacials.

Moreover, we show that these glacial-to-interglacial export production increases were accompanied by short-lived CaCO<sub>3</sub> spikes in these otherwise carbonate-poor sediments (Fig. 3D). We note that the preservation spike observed for the last glacial termination is muted at this site, for reasons that remain unclear. The near-absence of CaCO<sub>3</sub> in most of the record suggests that seafloor preservation of the CaCO<sub>3</sub> rain regulated the bimodal character of the record. Although intervals with higher sedimentary CaCO<sub>3</sub> concentrations could in principle reflect increased local CaCO<sub>3</sub> export, the abrupt increases and the transient nature of the CaCO<sub>3</sub> spikes compared to export production proxies argue instead for a deepening of the lysocline, as expected if CO<sub>2</sub> was lost from deep waters at this time.

The decrease in deep water exposure following peak interglacial conditions, indicated by declining export production, leads to CO<sub>2</sub> reduction, and this mechanism appears to apply in particular to the early stages of glaciation. As a general rule, elevated Antarctic export occurs during the peak interglacials, giving way to a major decline in the early stages of glaciation (Fig. 3 C), coinciding with the first half of the CO<sub>2</sub> decline into each glacial period, 40-50 ppm (Fig. 3A, reaching ~225 ppm). Remarkably, this is a similar, if slightly greater, reduction to the estimate from numerical models for the CO<sub>2</sub> decline that should result from a strong reduction in Antarctic overturning (Brovkin et al., 2007; Hain et al., 2011). While further declines in Antarctic export production occur later in the glacial progression (Fig. 3C), the associated CO<sub>2</sub> reduction associated with this mechanism should have nearly saturated (2). However, based on data from ODP Site 1090 in the Subantarctic Zone (SAZ) to the north of ODP Site 1094, it appears that the later stages of glaciation and climate cross a threshold at which the SAZ undergoes a dramatic rise in productivity (Fig. 3F) (6, 24) coincident with increased dust-borne iron supply to the SAZ from continental regions upstream in the westerly wind field (Fig. 3E; (7)). Iron fertilization in the SAZ would have permitted biological productivity in this

region to sequester additional regenerated carbon in the abyssal ocean, which would have further lowered atmospheric CO<sub>2</sub> (16, 25). It is again notable that numerical model simulations of Subantarctic iron fertilization predict roughly the observed CO<sub>2</sub> declines of ~ 40 ppm that occur later in the glacial progressions (21, 25, 26). In the modern ocean, there is upper ocean mixing across the fronts separating the AZ and SAZ (27). Thus, during peak ice conditions, iron fertilization in the SAZ may have further depleted the AZ of surface nutrients, contributing to the continued decline of AZ export production to its glacial minimum. In any case, it is a remarkable characteristic of the two records that the SAZ biological response begins when AZ productivity has reached the lower half of its range (Fig. 3C and F), with relatively little correlated variation between the AZ and SAZ (Fig. 4), and that the major changes in each correspond to roughly half of the observed CO<sub>2</sub> variation (Fig. 4). In summary, the paleoceanographic records from both the AZ and SAZ merge with the numerical model estimates of Southern Ocean to provide a coherent two-part Southern Ocean mechanism for the amplitude and timing of glacial interglacial CO<sub>2</sub> change.

The potential for these two modes of the Southern Ocean to have different roles in glacial/interglacial CO<sub>2</sub> change, first recognized in the context of the last glacial cycle (2, 16), is bolstered by the data reported here for the period of the “lukewarm” interglacials (MIS 13-19). The lukewarm interglacials are characterized by reduced amplitude of the ice-core  $\delta D$  and CO<sub>2</sub> records (Fig. 3) and a general decrease in global interglacial temperatures that appears to be more pronounced in Southern Ocean SST records (28). Given the potential dependencies of westerly wind position (29) and polar ocean water-column stability (30) on global temperature, the muting of the  $pCO_2$  increase during the lukewarm interglacials might have been linked to a reduced dynamic range of Antarctic overturning, with the abyssal ocean thereby maintaining a larger reservoir of regenerated carbon than in more recent interglacials (31). This hypothesis is supported by the Antarctic Ba/Fe record (Fig. 3C), which shows markedly reduced amplitude for the Ba/Fe maxima associated with the lukewarm interglacials (Fig. 4, squares with open circles along the x axis). Furthermore, this interval also generally has reduced deglacial CaCO<sub>3</sub> peaks (Fig. 3D), which would suggest that proportionally less CO<sub>2</sub> was released from the deep ocean. The expression of interglacials in the SAZ record is indistinguishable

between the period containing the lukewarm interglacials and the rest of the record (Figs. 3 & 4) (7, 24), suggesting that the cessation of SAZ iron fertilization occurred during the lukewarms as in other interglacials.

In contrast to the lukewarm interglacials, MIS 21 and 25 were characterized by full-amplitude export production peaks in the AZ accompanied by large  $\text{CaCO}_3$  preservation events, suggesting an increase in upwelling and deep-ocean  $\text{CO}_2$  release during Terminations X and XI (Fig. 3), consistent with planktic foraminiferal pH estimates that suggest that both interglacials had  $p\text{CO}_2$  values as high as recent interglacials (32). This observation further argues that the subsequent lukewarm interglacials represented a distinct period. Our observations thus indicate a strong coupling between Antarctic deep-to-surface exchange and the magnitude of the  $\text{CO}_2$  release from the ocean interior, which is consistent with observed changes in atmospheric  $p\text{CO}_2$  even beyond the interval covered by the Antarctic ice-core records.

There is much uncertainty and debate regarding the response of Southern Ocean overturning to ongoing global warming, as well to its impact on the oceanic uptake of anthropogenic  $\text{CO}_2$  (33). The paleoclimate data reported here argue strongly for a robust sensitivity of Antarctic overturning to global climate, in which overturning increases under warmer conditions. As the physical mechanism of this coupling is not yet clear, one cannot be confident that it will apply on the decadal to centennial scale and under the specific conditions of anthropogenic global warming. Nonetheless, the finding of stronger overturning under warmer climates, taken at face value, suggests a similar sense of change in the warmer future ocean.

## Figure captions

**Fig. 1** Core locations represented on the January-March sea-surface temperature field. The black line delineates maximum winter sea-ice extent (using the 90% winter sea-ice concentration line) based on the Hadley Center sea-ice concentration data 1978-2010 (34).

**Fig. 2** Biogenic particle flux reconstructed by  $^{230}\text{Th}$ -normalization for four independent

proxies covering the last two glacial terminations. Discrete measurements for the upper 25 kyrs have been performed on TN-57-13PC. (A) atmospheric  $p\text{CO}_2$  (1, 35); (B) comparison between  $\text{CaCO}_3$  flux and  $\text{Ca/Fe}$ ; (C) comparison between bioBa flux and  $\text{Ba/Fe}$ ; (D) chlorin flux; (E) biogenic opal flux. Blue shadings highlight ice ages, whereas red shadings indicate interglacials. The two arrows highlight the two step-transition into ice ages.

**Fig. 3** Records of (A) atmospheric  $p\text{CO}_2$  (1), (B) ODP 1094 planktic foraminifera  $\delta^{18}\text{O}$  (36, 37), (C) ODP 1094  $\text{Ba/Fe}$  (data smoothed by a five-point running mean), (D) ODP 1094  $\text{Ca/Fe}$  (data smoothed by a five-point running mean), (E) Fe flux to subantarctic core ODP1090 (7), and (F) ODP 1090 sedimentary alkenone concentration (24) covering the past 1 Myr. Red/grey shadings highlight intervals where Antarctic (AZ)/subantarctic (SAZ) processes, respectively, are dominantly controlling the partitioning of  $\text{CO}_2$  between the ocean interior and the atmosphere.

**Fig. 4** Comparison between ODP 1094  $\text{Ba/Fe}$  and ODP 1090 sedimentary alkenone concentration (24). Symbol colour indicates  $p\text{CO}_2$ . Filled circles illustrate the period 0-450 kyrs, filled squares the lukewarm interval (450-800 kyrs) and the open squares the interval 800-1000 kyrs for which  $p\text{CO}_2$  reconstruction do not yet exist.



## References and Notes

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